

pellet or particle form to be a reforming, water gas shift or dehydrogenation catalyst depending on the type of feedstocks fed in the inlet of the reactor and the type of reactions conducted within the catalytic zone, further, with hydrogen to be removed via permeation along the inner membrane tube, wherein the membrane is made by a metal, metal alloy, non-porous inorganic or metal-inorganic or composite material, with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols and non-permeate hydrogen to be rejected by the membrane and exit through the main outlet of the inner tube, with the permeate hydrogen to be diluted by a carrier gas flowing along the annular zone between inner and outer permeable tubes and further removed via permeation along the outer permeable membrane tube, wherein the outer membrane is made by a metal, metal alloy, non-porous inorganic or metal-inorganic or composite material, so that second permeate stream contains pure hydrogen only, with the annular space between the outer membrane tube and the far-outer impermeable tube which receives final permeate hydrogen to contain a selective catalyst, wherein permeate hydrogen reacts with a sweep component flowing through the inlet of this annular space in an exothermic type reaction and produces a product which exits via a separate outlet located by the end of the outer annular zone, with the heat generated by the exothermic reaction in the most-outer catalytic zone to be transferred via the radial direction into the main catalytic reaction zone of the inner membrane tube thus providing for part of the heat load necessary to drive the endothermic catalytic reactions within the inner membrane tube, with the main heating load of this inner zone to be achieved via heat transfer from the inner gas tubes which operate in the combustion regime by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air, and by flowing unreacted hydrocarbons, alcohols and carbon monoxide post-reaction species, and any of their mixtures, which are exiting from the inner membrane tube outlet and are recovered in the downstream of the reactor by use of separation processes including separation via membrane permeation, and by having these fuel gas mixtures to be recycled into the inlet of the heating tubes to support combustion and heat provision in the surrounding inner catalytic zone, finally with the sweep reactive component, which reacts with the hydrogen permeated via the outer membrane tube, to be one of the following:

an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a saturated hydrocarbon, such as ethane, propane, butane,

carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,

nitrogen for hydrogenation to ammonia,

a paraffin such as hexane for hydrocracking to a mixture of paraffins and olefins with a lower carbon atom, such as butane, propane, propylene, ethylene,

an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to a corresponding saturated component, such as conversion of cyclopentanone to cyclopentanol,

an aldehyde or ketone for reduction with hydrogen to the corresponding alcohol such as methanol, ethanol, propanol, butanol,

an alkyl or aryl halide for reduction with hydrogen to a corresponding non-halogen component,

a nitroalkane or aromatic nitro compound for reduction with hydrogen to a corresponding primary amine.

2. The process of claim 1, wherein the annular space enclosed between the outer permeable membrane tube and the far-outer impermeable metal tube is empty and the permeate pure hydrogen through outer membrane tube is used as feed in various consecutive applications including hydrogenation reactions for methanol, gasoline hydrocarbons, and ammonia synthesis, also as fuel in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

3. The process of claim 1 wherein the inner membrane tube is made by a porous inorganic, inorganic-metal or composite membrane material with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, steam, reactant and product hydrocarbons and alcohols to permeate also through the membrane in a lesser

degree, with hydrogen only to permeate through the outer membrane tube and with the remaining non-permeate species to exit through the reject outlet of the annular space created between the two membrane tubes either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate pure hydrogen through the outer membrane to be used as feed in various consecutive applications including hydrogenation reactions for methanol, gasoline hydrocarbons and ammonia synthesis, also as fuel in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

4. The process of claim 1 as applied to carbon dioxide hydrocarbon reforming and dehydrogenation reactions, wherein the inner membrane tube is made by a porous inorganic, inorganic-metal or composite membrane material with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, reactant and product hydrocarbon species, to permeate also through the membrane in a lesser degree, and with the outer membrane tube to be made by an organic, inorganic, or composite polymer membrane which withstands high temperatures and is permselective to both hydrogen and carbon dioxide species, with hydrogen and carbon dioxide for the reforming reaction or hydrogen only for the dehydrogenation reaction, to permeate through the outer membrane, and with the remaining non-permeate species to exit through the reject outlet of the annular space created between the two membrane tubes, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the outer membrane hydrogen and carbon dioxide mixture to be used for methanol synthesis or as feed in molten carbonate fuel cells, and in case wherein hydrogen only is the permeate through same membrane to be used as feed in various consecutive applications including hydrogenation reactions for methanol, gasoline hydrocarbons, and ammonia synthesis, also as fuel in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

5. A process for conducting catalytic steam and CO₂ hydrocarbon reforming, steam-alcohol reforming, water gas shift, and dehydrogenation reactions for production and use of hydrogen and synthesis gas which includes:

a most outer non-permeable tubular cylinder which is hollow in the center and nests two more concentric hollow membrane tubular cylinders, a next-inner one and a most-inner one, which are both made by permeable materials with the annular space between most-outer and next-inner cylinders to contain a metallic catalyst in the form of pellets or particles, with the catalyst to be a reforming, water gas shift or dehydrogenation catalyst depending on the feedstocks fed in the inlet of the annular catalytic zone and the type of reactions conducted within the catalytic zone, with the next-inner cylinder to nest also a concentric most-inner hollow membrane cylinder, with next-inner cylinder to be made by a metal, metal alloy, non-porous inorganic, or composite material which is permeable only to hydrogen, with product hydrogen from the catalytic reaction zone to permeate through the lateral membrane surface of next-inner cylinder, with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols and non-permeate hydrogen to be rejected by the next-inner membrane and exit through outlet fitting ports located by the end of the outer catalytic zone, with permeate hydrogen flowing along the annular zone between next-inner and most-inner cylinders to be diluted by a carrier gas flowing along the same annular space and further removed via permeation across the most-inner permeable membrane tube, wherein most-inner membrane tube is made by metal, metal-alloy, non-porous inorganic or composite materials, so that secondly permeated stream flowing inside most-inner membrane tube contains only pure hydrogen, with most-inner membrane tube to contain a selective catalyst in form of particles or pellets, wherein permeate hydrogen reacts with a sweep component flowing through the inlet port of the most-inner membrane tube in an exothermic type reaction and produces a product which exits via a separate outlet located by the end of the most inner cylinder, with the heat generated by the exothermic reaction to be transferred into the main catalytic reaction zone enclosed between most-outer and next-inner hollow cylinders, thus providing for part of the heat load necessary to drive the endothermic catalytic reactions occurring in

this zone, with the main heating of the overall cylindrical assembly and of main catalytic zone to be achieved by heat transfer coming from combustion of gases, including combustion of waste type hydrocarbons and hydrocarbon-hydrogen mixtures mixed with oxygen or air, also of unreacted hydrocarbons, alcohols, and carbon monoxide post-reaction species and any of their mixtures exiting from the corresponding outlet port of outer cylinder and recovered in the downstream of the reactor by use of separation processes including separation via membrane permeation, which are recycled as fuel gas flowing along the external side of most-outer impermeable cylinder to support combustion and heat provision in enclosed main catalytic zone, and finally with the sweep reactive component which reacts with the hydrogen permeated via the most-inner membrane tube, to be one of the following:

- an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a saturated hydrocarbon, such as ethane, propane, butane,
- carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,
- nitrogen for hydrogenation to ammonia,
- a paraffin such as hexane for hydrocracking to a mixture of paraffins and olefins with a lower carbon atom, such as butane, propane, propylene, ethylene,
- an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,
- an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to a corresponding saturated component, such as conversion of cyclopentanone to cyclopentanol,
- an aldehyde or ketone for reduction with hydrogen to the corresponding alcohol such as methanol, ethanol, propanol, butanol,
- an alkyl or aryl halide for reduction with hydrogen to a corresponding non-halogen component,
- a nitroalkane or aromatic nitro compound for reduction with hydrogen to a corresponding primary amine.

6. The process of claim 5, wherein most inner membrane tube is empty and the pure permeate hydrogen within this tube is used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons, and ammonia synthesis, also as fuel in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

7. The process of claim 5 wherein next-inner membrane cylinder is made by a porous inorganic or inorganic-metal or composite membrane, with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, steam, reactant and product hydrocarbons and alcohols, to permeate also through the membrane in a lesser degree, with hydrogen only to permeate through the most-inner membrane tube and with the remaining non-permeate species, to exit through the reject outlet of the annular space created between next-inner and most-inner cylinders, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the inner membrane tube, pure hydrogen product, to be used as feed in various consecutive applications including hydrogenation reactions for methanol, gasoline hydrocarbons and ammonia synthesis, also as fuel in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

8. The process of claim 7, as applied to carbon dioxide hydrocarbon reforming and dehydrogenation reactions only, wherein the most-inner membrane tube is made by an organic, inorganic, or composite polymer membrane which withstands high temperature and is permselective to both hydrogen and carbon dioxide species which permeate through the most-inner membrane tube, with the remaining non-permeate species to exit through the reject outlet of the annular space created between the next-inner and most-inner membrane tubes either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the most-inner membrane tube hydrogen and carbon dioxide mixture to be used for methanol synthesis

and as feed in molten carbonate fuel cells, and in reaction case wherein hydrogen only permeates through the most-inner membrane tube, permeate hydrogen is used as feed in various consecutive applications including hydrogenation reactions for methanol, gasoline hydrocarbons, and ammonia synthesis, and as fuel in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

9. The process of claim 3, as applies to steam and CO₂ hydrocarbon reforming reactions, with H₂ and CO to be produced via hydrocarbon steam reforming, hydrocarbon CO₂ reforming, and water gas shift reactions, with the final permeate stream to contain pure hydrogen product permeated through the far outer membrane tube, with the reject exit stream from the permreactor which contains carbon monoxide and non-permeate hydrogen product, unreacted hydrocarbons, carbon dioxide, and steam to be passed through a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and into any subsequently placed steam reforming reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

- organic polymer membrane,
- inorganic membrane,
- composite inorganic-metal-organic membrane,
- composite organic-inorganic membrane,
- composite organic-metal membrane,
- composite inorganic-metal membrane,

which all materials are permselective to H₂ and CO₂ and separate these two species in permeate stream from the unreacted hydrocarbons and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the H₂ and CO₂ permeate mixture to be used for methanol synthesis and as fuel in molten carbonate fuel cells, also in other

chemical synthesis and
fuel type reactions
either as a mixture or after the CO₂ condensation and removal, as pure hydrogen, either
as single stream of hydrogen or
as combined stream of hydrogen after its combination with the stream of
hydrogen permeated from the first permreactor.

10. The process of claim 9 wherein the hydrocarbon is a single constituent or a mixture of constituents of the following components:

methane,
ethane,
propane,
n-butane,
i-butane,
methanol,
ethanol,
propanol,
butanol,
naphtha,
gasoline,
natural gas rich in methane,
coal gas rich in methane,
landfill gas rich in methane,
flue gas rich in methane,
biomass gas rich in methane,

and wherein the combined hydrocarbon and carbon dioxide gas mixture is substituted by:

a CH₄ and CO₂ mixture,
acidic natural gas rich in CH₄ and CO₂,
coal gas rich in CH₄ and CO₂,
landfill gas rich in CH₄ and CO₂,

biomass gas rich in CH₄ and CO₂,

other primary, secondary, refinery, and flue gas mixtures rich in CH₄ and CO₂.

11. The process of claim 7, as applies to steam and CO₂ hydrocarbon reforming reactions, with H₂ and CO to be produced via hydrocarbon steam reforming, hydrocarbon CO₂ reforming, and water gas shift reactions, with the final permeate stream to contain pure hydrogen product, permeated through the most inner membrane tube, with the reject exit stream from the permreactor which contains carbon monoxide and non-permeate hydrogen product, unreacted hydrocarbons, carbon dioxide and steam to be passed through a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,

inorganic membrane,

composite inorganic-metal membrane,

composite inorganic-metal-organic membrane,

composite organic-inorganic membrane,

composite organic-metal membrane,

which all materials are permselective to H₂ and CO₂ and separate these two species in the permeate stream from the unreacted hydrocarbons and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the H₂ and CO₂ permeate mixture to be used for methanol synthesis, and as fuel in molten carbonate fuel cells, also for other

chemical synthesis and

fuel type reactions

either as a mixture or after the CO₂ condensation and removal, as pure hydrogen, either as single stream of hydrogen or

as combined stream of hydrogen after its combination with the stream of hydrogen permeated from the first permreactor.

12. The process of claim 11 wherein the hydrocarbon is a single constituent or a mixture of constituents of the following components:

- methane,
- ethane,
- propane,
- n-butane,
- i-butane,
- methanol,
- ethanol,
- propanol,
- butanol,
- naphtha,
- gasoline,
- natural gas rich in methane,
- coal gas rich in methane,
- landfill gas rich in methane,
- flue gas rich in methane,
- biomass gas rich in methane,

and wherein the combined hydrocarbon and carbon dioxide gas mixture is substituted by:

- a CH_4 and CO_2 mixture,
- acidic natural gas rich in CH_4 and CO_2 ,
- coal gas rich in CH_4 and CO_2 ,
- landfill gas rich in CH_4 and CO_2 ,
- biomass gas rich in CH_4 and CO_2 ,
- other primary, secondary, refinery, and flue gas mixtures rich in CH_4 and CO_2 .

13. The process of claim 9, with the reject stream from the permeator containing unreacted hydrocarbons and CO to enter into a consecutively placed steam reformer to react with steam over a bed of metallic catalyst via the steam reforming and water gas shift reactions and be converted into H₂ and CO₂ products, having this exit stream from last reformer to condense its unreacted steam by passage through a heat exchanger and by generating new steam in other side of the heat exchanger which is used as feed into the inlet of this last reformer, having the final exit dry mixture of H₂ and CO₂ from the heat exchanger to be combined with the permeate from the membrane permeator H₂ and CO₂ stream, to make one combined stream of H₂ and CO₂ to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis

and fuel type reactions

either as a mixture or after the CO₂ condensation and removal, as pure hydrogen, either as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permreactor.

14. The process of claim 11, with the reject stream from the permeator containing unreacted hydrocarbons and CO to enter into a consecutively placed steam reformer to react with steam over a bed of metallic catalyst via the steam reforming and water gas shift reactions and be converted into H₂ and CO₂ products, having this exit stream from last reformer to condense its unreacted steam by passage through a heat exchanger and by generating new steam in other side of the heat exchanger which is used as feed into the inlet of this last reformer, having the final exit dry mixture of H₂ and CO₂ from the heat exchanger to be combined with the permeate from the membrane permeator H₂ and CO₂ stream, to make one combined stream of H₂ and CO₂ to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis
and fuel type reactions
either as a mixture or after the CO₂ condensation and removal, as pure hydrogen, either
as single hydrogen stream or
as combined hydrogen stream after its combination with the hydrogen stream
permeated from the first permreactor.

15. The process of claim 11 wherein the membrane in permeator is made from an organic polymer or composite or copolymer of organic polymers selected from the group of the following:

- polyimides,
- polycarbonates,
- polysulfones,
- polybenzimidazoles,
- polyphosphazenes,
- polyamides,
- polystyrenes,
- polycaprolactams,
- parylenes,
- polyvinyl halides,
- polyacetates,
- polysiloxanes

or with the membrane in permeator to be made from inorganic-organic composite materials made by a mixture of one or more of the above polymers with one or more of the following ceramic oxides:

- alumina (Al₂O₃),
- titania (TiO₂),
- silica (SiO₂),
- zirconia (ZrO₂),

or with the membrane in permeator to be made from inorganic-metal materials made by a mixture of one or more metals with one or more of the above ceramic oxides, or with the membrane in permeator to be made from inorganic only materials made by a mixture of one or more of the above ceramic oxides.

16. The process of claim 9 wherein the permeator which follows the first permreactor is replaced by a permreactor of a simple membrane reactor structure consisting of a permeable membrane tube filled with proper catalyst, so that when conversion is high in first permreactor and product is rich in CO, the second permreactor is used to conduct the catalytic water gas shift reaction only with H₂ and CO₂ products, and further, when the conversion is low in first permreactor wherein exit stream from first permreactor contains significant amounts of unreacted hydrocarbons and carbon dioxide, to conduct in second permreactor, after addition of steam in the feed, the hydrocarbon steam reforming and hydrocarbon carbon dioxide reforming reactions together with the water gas shift reaction over a bed of metallic catalyst with H₂ and CO products to be produced in second case,

with the membrane in second permreactor to be made by one of the following materials:

metal or metal alloy membrane,

non-porous inorganic membrane,

composite membrane,

with all above materials to be permselective for H₂ and separate only H₂ in permeate stream of second permreactor from the unreacted CO, steam and product CO₂ in first case, or from the unreacted mixture of hydrocarbons, steam, CO₂, and CO in second case, with all gases to exit from the non-permeate side of the permreactor as a reject stream, which after the steam removal, can be recycled as feed into the first permreactor if it is rich in CO₂ as in first case, with the permeate from the membrane H₂ to be used in

chemical synthesis

and fuel type reactions

either, as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream which permeates from the first catalytic permreactor.

17. The process of claim 11 wherein the permeator which follows the first permreactor is replaced by a permreactor of a simple membrane reactor structure consisting of a permeable membrane tube filled with proper catalyst, so that when conversion is high in first permreactor and product is rich in CO, the second permreactor is used to conduct the catalytic water gas shift reaction only with H₂ and CO₂ products, and further, when the conversion is low in first permreactor wherein exit stream from first permreactor contains significant amounts of unreacted hydrocarbons and carbon dioxide, to conduct in second permreactor, after addition of steam in the feed, the hydrocarbon steam reforming and hydrocarbon carbon dioxide reforming reactions together with the water gas shift reaction over a bed of metallic catalyst with H₂ and CO products to be produced in second case,

with the membrane in second permreactor to be made by one of the following materials:

metal or metal alloy membrane,

non-porous inorganic membrane,

composite membrane,

with all above materials to be permselective for H₂ and separate only H₂ in permeate stream of second permreactor from the unreacted CO, steam and product CO₂ in first case, or from the unreacted mixture of hydrocarbons, steam, CO₂, and CO in second case, with all gases to exit from the non-permeate side of the permreactor as a reject stream, which after the steam removal, can be recycled as feed into the first permreactor if it is rich in CO₂ as in first case, with the permeate from the membrane H₂ to be used in

chemical synthesis

and fuel type reactions

either, as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream which permeates from the first catalytic permreactor.

18. The process of claim 9 wherein the feed stream into first permreactor consists of a hydrocarbon and carbon dioxide or a mixture of hydrocarbons and carbon dioxide, reformed over a bed of metallic catalyst with CO₂ hydrocarbon reforming reactions and the reverse water gas shift reaction to take place and to produce H₂ and CO products.

19. The process of claim 11 wherein the feed stream into first permreactor consists of a hydrocarbon and carbon dioxide or a mixture of hydrocarbons and carbon dioxide, reformed over a bed of metallic catalyst with CO₂ hydrocarbon reforming reactions and the reverse water gas shift reaction to take place and to produce H₂ and CO products.

20. The process of claim 9 wherein the combined H₂ and CO₂ product mixture from the permeator is used:

- (a) for direct methanol synthesis via the reaction: CO₂+3H₂=CH₃OH+H₂O,
- (b) for direct feed in molten carbonate fuel cell (MCFC) units for electricity generation via the overall electrochemical reaction: H₂+CO₂+1/2O₂(cathode) \rightarrow H₂O+CO₂(anode),
- (c) for other CO₂ and H₂ direct combination reaction including the one that produces formic acid,

Further, after the removal of CO₂ by condensation, the generated pure H₂ is combined with pure H₂ coming out of the first reforming reactor and used:

- (d) as fuel feed in hydrogen based fuel cell units including molten carbonate, solid oxide, proton exchange, alkaline, phosphoric type,
- (e) as fuel feed in gas turbines, conventional and jet type gas engines,
- (f) as synthesis reactant in consecutive hydrogenation reactions including these for methanol, ammonia and gasoline hydrocarbon synthesis, also these for saturation of unsaturated hydrocarbons including alkenes to alkanes, alkynes to alkenes and further to alkanes, also these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, also these for reduction of alkyl

and aryl halides, and these for reduction of nitroalkanes and aromatic nitro compounds into corresponding primary amines.

21. The process of claim 11 wherein the combined H₂ and CO₂ product mixture from the permeator is used:

- (a) for direct methanol synthesis via the reaction: CO₂+3H₂=CH₃OH+H₂O,
- (b) for direct feed in molten carbonate fuel cell (MCFC) units for electricity generation via the overall electrochemical reaction: H₂+CO₂+1/2O₂(cathode) \rightarrow H₂O+CO₂(anode),
- (c) for other CO₂ and H₂ direct combination reaction, including the one that produces formic acid,

further, after the removal of CO₂ by condensation, the generated pure H₂ is combined with pure H₂ coming out of the first reforming permreactor and used:

- (d) as fuel feed in hydrogen based fuel cell units including molten carbonate, solid oxide, proton exchange, alkaline, phosphoric type,
- (e) as fuel feed in gas turbines, conventional and jet type gas engines,
- (f) as synthesis reactant in consecutive hydrogenation reactors including these for methanol, ammonia and gasoline hydrocarbon synthesis, also these for saturation of unsaturated hydrocarbons including alkenes to alkanes, alkynes to alkenes to alkanes, also these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, also these for reduction of alkyl and aryl halides, and these for reduction of nitroalkanes and aromatic nitro compounds into corresponding primary amines.

22. The process of claim 11 wherein the feed stream into the first permreactor consists only of a carbon monoxide and steam (H₂O(g)) mixture, reacting over a bed of metallic catalyst to produce H₂ and CO₂ via the water gas shift reaction alone, with hydrogen to permeate through the most-inner membrane tubes and with the remaining components including unreacted carbon monoxide, steam, carbon dioxide product and

non-permeate hydrogen to exit through the reject stream of the outer cylinder and enter into the consecutive permeator.

23. The process of claim 22 with the reject stream from the permeator containing the non-permeate, unreacted CO to be recycled into the inlet of first water gas shift permreactor for continuous water gas shift reaction into the main catalytic zone.

24. The process of claim 23 with the reject stream from the permeator containing non-permeate, unreacted CO to enter into a consecutive placed water gas shift reactor to react with steam over a bed of metallic catalyst via the water gas shift reaction and be converted into H₂ and CO₂ products, having the exit stream from last shift reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in the other side of the heat exchanger to be used as feed in the inlet of this last shift reactor in an autothermic type of operation, having the final exit dry mixture of H₂ and CO₂ from last heat exchanger to be combined with the permeate from the membrane permeator H₂ and CO₂ stream, to make a combined stream for use as feed in methanol synthesis and molten carbonate fuel cells, also in other,

chemical synthesis

and fuel type reactions

either as it is mixture or after the CO₂ condensation and removal, as pure hydrogen, either

as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permreactor.

25. The process of claim 3, as applies to dehydrogenation reactions of alkanes, with the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to

contain pure hydrogen product permeated through the most-inner membrane tube and with the exit reject stream from the permreactor which contains product alkenes, non-permeate hydrogen and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which can be used as feed into any steam requiring process with the exit from the heat exchanger species such as alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

- organic polymer membrane,
- inorganic membrane,
- inorganic-metal membrane,
- composite inorganic-metal-organic membrane,
- composite inorganic-organic membrane,
- composite metal-organic membrane,
- metal or metal alloy membrane,
- carbon membrane,

which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream which is to be used for:

- a) polyolefin synthesis in consecutive polymerization reactors,
- b) oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene oxide, ethylene glycol, propylene oxide, propylene glycol, ethanol, propanol, isopropanol, butanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated through the first permeable reactor, in:

- chemical synthesis,
- and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

26. The process of claim 7, as applies to dehydrogenation reactions of alkanes, with the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to contain pure hydrogen product permeated through the most-inner membrane tube and with the exit reject stream from the permreactor which contains product alkenes, non-permeate hydrogen and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which can be used as feed into any steam requiring process with the exit from the heat exchanger species such as alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

- organic polymer membrane,
- inorganic membrane,
- inorganic-metal membrane,
- composite inorganic-metal-organic membrane,
- composite inorganic-organic membrane,
- composite metal-organic membrane,
- metal or metal alloy membrane,
- carbon membrane,

which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream which is to be used for:

- a) polyolefin synthesis in consecutive polymerization reactors,
- b) oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene oxide, ethylene glycol, propylene oxide, propylene glycol, ethanol, propanol, isopropanol, butanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen

stream after its combination with the hydrogen stream permeated through the first permeable reactor, in:

chemical synthesis,

and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

27. The process of claim 26 wherein the alkane hydrocarbon is a single constituent or a mixture of constituents of the following components:

ethane,

propane,

n-butane,

i-butane,

natural gas rich in ethane and propane,

naphtha,

gasoline,

refinery gas rich in ethane,

refinery gas rich in propane,

refinery gas rich in butane,

refinery gas rich in isobutane,

refinery gas rich in ethane, propane, butane, isobutane,

a primary, secondary, or flue gas rich in ethane, propane, butane, isobutane.

28. The process of claim 26 wherein the membrane in permeator is made from an organic polymer or composite or copolymer of organic polymers selected from the group of the following:

polyimides,

polycarbonates,

polysulfones,
polybenzimidazoles,
polyphosphazenes,
polyamides,
polystyrenes,
polycaprolactams,
parlenes,
polyvinyl halides,
polyacetates,
polysiloxanes,

or with the membrane in permeator to be made from inorganic-organic composite materials made by a mixture of one or more of the above polymers with one or more of the following ceramic oxides:

alumina (Al_2O_3),
titania (TiO_2),
silica (SiO_2),
zirconia (ZrO_2),

or with the membrane in permeator to be made from inorganic-metal materials made by a mixture of one or more metals with one or more of the above ceramic oxides,
or with the membrane in permeator to be made from inorganic only materials made by a mixture of one or more of the above ceramic oxides,
or with the membrane in permeator to be made from metal and metal alloys materials comprising by one or more of the following metals:

Palladium (Pd),
Vanadium (V),
Platinum (Pt),
Silver (Ag),
Chromium (Cr),
Copper (Cu),
Iron (Fe),

Nickel (Ni).

29. The process of claim 9 wherein the feed stream into the first permreactor consists only of a hydrocarbon and steam ($H_2O(g)$) mixture or an alcohol and steam mixture, or a combined hydrocarbon, alcohol and steam mixture, reacting over a bed of metallic catalyst to produce H_2 , CO_2 and traces of CO via the hydrocarbon steam reforming, alcohol steam reforming, and water gas shift reactions, with hydrogen to permeate through the outer membrane tube and with the remaining components including unreacted hydrocarbons, alcohols, steam, carbon dioxide, carbon monoxide, and non-permeate hydrogen to exit through the reject stream of the inner cylinder, and with the combined hydrogen and carbon dioxide product mixture to be removed in the consecutive permeator via membrane permeation.

30. The process of claim 11 wherein the feed stream into the first permreactor consists only of a hydrocarbon and steam ($H_2O(g)$) mixture or an alcohol and steam mixture, or a combined hydrocarbon, alcohol and steam mixture, reacting over a bed of metallic catalyst to produce H_2 , CO_2 and traces of CO via the hydrocarbon steam reforming, alcohol steam reforming and water gas shift reactions, with hydrogen to permeate through the inner membrane tube and with the remaining components including unreacted hydrocarbons, alcohols, steam, carbon dioxide, carbon monoxide, and non-permeate hydrogen to exit through the reject stream of the outer cylinder, and with the combined hydrogen and carbon dioxide product mixture to be removed in the consecutive permeator via membrane permeation.

31. The process of claim 29 with the reject stream from the permeator containing non-permeate, unreacted hydrocarbons and product CO, or unreacted alcohols and product CO, or unreacted hydrocarbons, alcohols and CO, to be recycled into the inlet of first permreactor for continuous hydrocarbon-steam reforming, alcohol steam reforming, and water gas shift reactions taking place into the main catalytic zone of the reformer.

32. The process of claim 30 with the reject stream from the permeator containing non-permeate, unreacted hydrocarbons and product CO or unreacted alcohols and product CO, or unreacted hydrocarbons, alcohols and CO, to be recycled into the inlet of first permreactor for continuous hydrocarbon-steam reforming, alcohol steam reforming, and water gas shift reactions taking place into the main catalytic zone of the reformer.

33. The process of claim 32 wherein the first permeable reformer is replaced by a simple tubular catalytic reactor so that all reaction products and unreacted reactants are exiting from a single outlet and directed into the consecutive permeator, with the process to include recycling of non-permeate alcohols, hydrocarbons and carbon monoxide into the reformer for continuous reaction.

34. The process of claim 32 wherein the first permeable reformer is replaced by a simple membrane reactor which consists of a simple tubular membrane reactor with a catalytic zone within, to conduct combined alcohol steam reforming and water gas shift reactions only, with permeate hydrogen only to be removed continuously from the membrane of the membrane reactor and with the process to include a recycling stream from the consecutive permeator for the non-permeate alcohols and carbon monoxide back into the inlet of the membrane reactor for continuous reaction.

35. The process of claim 30 with the reject stream from the permeator containing non permeate unreacted hydrocarbons, alcohols and CO, or alcohols and CO, to enter into a consecutive placed reformer to react with steam over a bed of metallic catalyst via the alcohol, hydrocarbon steam reforming and water gas shift reactions and be converted into H₂, CO₂ product mixture, having the exit stream from last reforming reactor to condense its unreacted steam by passing through a heat exchanger and by generating new steam in other side of the heat exchanger to be used as feed into the inlet of the last reformer in an autothermic type of operation, having the final exit dry mixture of H₂ and

CO₂ from last heat exchanger to be combined with the permeate from the membrane permeator H₂ and CO₂ stream, to make a combined gas stream for use as feed in a methanol synthesis reactor, or formic acid synthesis reactor, or in a molten carbonate fuel cell unit, or in other,

chemical synthesis

and fuel type reactions

either as it is mixture or after condensation and removal of CO₂, as pure hydrogen, either,

as single hydrogen stream, or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reformer.

36. The process of claim 11 wherein the membrane permeator following the permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the unreacted steam, hydrocarbons, alcohols, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons, alcohols, and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously or periodically reheated by use of an immersed or surrounding heater to the lower section of the separator containing the liquified phase, and to be exited from the separator by use of a special open-close valve, and be recycled into the inlet of the first reforming reactor for continuous conduction of the steam and carbon dioxide reforming and water gas shift reactions in the reformer, with the separated gaseous hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications:

- a) methanol synthesis,
- b) gasoline synthesis via Fischer-Tropsch synthesis route,
- c) as combustion fuel or as combustion fuel blending in gas turbines and gas engines,

- d) as fuel in solid oxide fuel cells,
- e) as fuel in molten carbonate fuel cells,
either as is it mixture, or after mixing with all or part of the hydrogen stream permeated from the permeable reformer.

37. The process of claim 19 wherein the membrane permeator following the permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the unreacted steam, hydrocarbons, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons, and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously or periodically reheated by use of an immersed or surrounding heater to the lower section of the separator containing the liquified phase, and to be exited from the separator by use of a special open-close valve, and be recycled into the inlet of the first reforming reactor for continuous conduction of the steam and carbon dioxide reforming and water gas shift reactions in the reformer, with the separated gaseous hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications:

- a) methanol synthesis,
- b) gasoline synthesis via Fischer-Tropsch synthesis route,
- c) as combustion fuel or as combustion fuel blending in gas turbines and gas engines,
- d) as fuel in solid oxide fuel cells,
- e) as fuel in molten carbonate fuel cells,
either as is it mixture, or after mixing with all or part of the hydrogen stream permeated from the permeable reformer.

38. The process of claim 36, wherein the permreactor is replaced by a simple tubular catalytic reactor which is non-permeable and includes only one exit stream which is rich in hydrogen, carbon monoxide products and unreacted steam, hydrocarbons, alcohols, carbon dioxide, with this single exit stream to be fed into the cryogenic separator after the removal of steam in the previous heat exchanger.

39. The process of claim 11 wherein the membrane permeator following the permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the unreacted steam, hydrocarbons, alcohols, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously reheated by use of an immersed or surrounding heater to the section of the separator containing the liquified phase, and to be exited from the separator by use of a special open-close valve, and be fed into the inlet of a consecutive reforming reactor for continuous steam, carbon dioxide reforming and water gas shift reactions in the reformer and conversion into final H₂ and CO₂ products, having the exit stream from the last reforming reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in the other side of the heat exchanger to be used as additional steam feed in the inlet of the last reforming reactor in an autothermic type of operation, having the final exit dry mixture of H₂ and CO₂ from last heat exchanger to be used as direct feed in a methanol synthesis reactor and a molten carbonate fuel cell unit, or in other

chemical synthesis reactions including formic acid synthesis,

and in fuel type reactions,

either as it is mixture or after the CO₂ condensation and removal, as pure hydrogen, moreover with the separated hydrogen and carbon monoxide gas mixture from the cryogenic separator to be used in the following applications:

a) methanol synthesis,

- b) gasoline synthesis via Fischer-Tropsch synthesis route,
- c) as combustion fuel or as combustion fuel blending in gas turbines and gas engines,
- d) as fuel in solid oxide fuel cells,
- e) as fuel in molten carbonate fuel cells,

either as is it mixture, or after mixing with part or all of the hydrogen stream permeated from the first permeable reformer.

40. The process of claim 7 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide only reforming of hydrocarbons, including methane as a hydrocarbon, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen, carbon monoxide products and unreacted steam, which exit rejected stream enters as a fuel feed into a solid oxide fuel cell unit for electricity or power generation, and with part or all of the permeate hydrogen coming out of the separate permreactor exit to be recycled into the reject exit stream from the permreactor, in order to provide for additional hydrogen fuel entering into the solid oxide fuel cell unit.

41. The process of claim 40 wherein the first permreactor is replaced by a simple tubular catalytic reactor which is non-permeable and includes only one exit stream which is rich in hydrogen, carbon monoxide and steam and is fed directly as fuel into the solid oxide fuel cell unit.

42. The process of claim 3 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide only reforming of hydrocarbons, including methane as a hydrocarbon, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen, carbon monoxide products and unreacted steam, which exit rejected stream enters as a fuel feed into a solid oxide fuel cell unit for electricity or power generation,

and with part or all of the permeate hydrogen coming out of the separate permreactor exit to be recycled into the reject exit stream from the permreactor, in order to provide for additional hydrogen fuel entering into the solid oxide fuel cell unit.

43. The process of claim 7 as applied to the steam reforming of hydrocarbons and alcohols to occur within the permreactor either as a separate reaction or as combined reactions, including methane as a hydrocarbon and methanol, ethanol as alcohols, wherein complete conversion of hydrocarbons and alcohols occurs in the permeable catalytic reformer and the reject exit stream from the reformer consists only of hydrogen, carbon dioxide products and unreacted steam, which this exit rejected stream to be fed as fuel into a molten carbonate fuel cell unit for electricity or power generation, and with part or all of the permeate hydrogen coming out of the separate permreactor exit to be recycled into the reject exit stream from the permreactor, in order to provide for additional hydrogen fuel entering into the molten carbonate fuel cell unit.

44. The process of claim 43 wherein the first permreactor is replaced by a simple tubular catalytic reactor which is non-permeable and includes only one exit stream which is rich in hydrogen, carbon dioxide and steam and is fed directly as fuel into a molten carbonate fuel cell unit.

45. The process of claim 7 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide only reforming of hydrocarbons, wherein a high conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer, so that the reject exit stream from the reformer contains non-permeate hydrogen product, carbon monoxide product, traces of unreacted hydrocarbons, carbon dioxide and unreacted steam, which stream enters into a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming or water gas shift reactor, with the exit stream from the heat exchanger to be passed

through a bed of moisture adsorbing particles to remove any moisture content, with the dry exit gas mixture to enter into a methanol synthesis catalytic reactor which produces methanol in the gas or liquid phase, depending on reaction conditions and catalyst used, by reacting hydrogen with carbon monoxide and any containing carbon dioxide over a metallic catalyst, with part or all of the pure hydrogen produced in the permeator to be used for complementing the hydrogen gas fed into the methanol reactor, with the methanol product stream exiting from the synthesis reactor to be used as a whole or part as fuel into a methanol driven fuel cell unit for electricity or power generation.

46. The process of claim 26, wherein the membrane in the downstream membrane permeator is replaced by an alkene selective membrane so that alkene is separated in the permeate stream from the alkane-alkene mixture which is entering into the permeator from the preceded permreactor, with the rejected alkane stream to be recycled into the inlet of the permreactor for continuous reaction, with the alkene selective membrane to be made by a polymer-metal or composite material with metals such as silver, copper, zinc, chromium, platinum, palladium, zirconium.

47. A process for conducting catalytic hydrocarbon dehydrogenation coupled with catalytic hydrogenation reactions, and catalytic hydrocarbon and alcohol steam, CO₂ reforming coupled with hydrogenation reactions, with permeation of hydrogen via inner selective membranes, which includes:

a far-outer impermeable hollow tubular cylinder which nests two more concentric permeable tubular cylinders, a next inner and a most inner one, with the central annular zone created between the inner and most inner membrane cylinders to be filled with a dehydrogenation or reforming catalyst based on nickel, rhodium, ruthenium, chromium, platinum, palladium, silver, in form of pellets or particles, with tubular-inner type heaters to run axially along the central annular zone to provide necessary endothermic heat for the reaction, with the most inner permeable cylinder to be filled with a hydrogenation catalyst based on copper, chromium, zinc, tin, iron, palladium, platinum, nickel, rhodium, ruthenium, silver, cobalt, sodium, potassium, calcium, boron, barium, lithium,

in form of pellets or particles, with the same hydrogenation catalyst to fill also the space between the next inner and outer tubes, with hydrogen permselective membranes to comprise the membrane tubes, with the membranes to be made from metal, metal alloys, inorganic, inorganic-metal or composite materials, with hydrogen to be generated in the central annular zone from a dehydrogenation or reforming reaction and permeate via the next inner and most-inner membranes into the corresponding opposite tubular compartments, with a sweep compound to flow in the most inner and outer annular zones and with the permeate hydrogen to react with the sweep compound in the respective catalytic zone, in exothermic hydrogenation type reactions, which include:

- (a) hydrogenation reactions of hydrogen with an aldehyde or ketone to form a corresponding alcohol such as methanol, ethanol, propanol, butanol,
- (b) hydrocracking of hydrogen with a paraffin to form a mixture of paraffins and olefins with a lower carbon atom, such hydrocracking of hexane to form butane, propane, propylene, ethylene,
- (c) hydrogenation reactions of hydrogen with an unsaturated hydrocarbon such as an alkene or alkyne to form a saturated hydrocarbon, such as ethane, propane, butane,
- (d) carbon monoxide reactions with hydrogen to form methanol or gasoline hydrocarbons,
- (e) nitrogen hydrogenation to ammonia,
- (f) reduction of an aromatic hydrocarbon with hydrogen to form a non-aromatic hydrocarbon,
- (g) hydrogenation of an unsaturated alcohol, phenol, aldehyde, ketone, or acid with hydrogen to form a corresponding saturated component, such as this of cyclopentanone to cyclopentanol,
- (h) hydrogenation of an alkyl or aryl halide with hydrogen to form a corresponding non-halogen component,
- (i) hydrogenation of a nitroalkane or aromatic nitro compound with hydrogen to form a corresponding primary amine,

with the olefin product to exit from the outlet of the central annular zone, and the hydrogenation products to exit from the outlets of the most inner and outer annular zones.

48. The process of claim 47 wherein the paraffin hydrocarbon flowing in the central annular zone which undergoes dehydrogenation reaction is a single constituent or a mixture of constituents of the following components:

methane,
ethane,
propane,
n-butane,
i-butane,
natural gas rich in ethane and propane,
naphtha,
gasoline,
refinery gas rich in ethane,
refinery gas rich in propane,
refinery gas rich in butane,
refinery gas rich in isobutane,
refinery gas rich in ethane, propane, butane, isobutane,
primary, secondary, and flue gas mixtures rich in ethane, propane, butane,
isobutane.

49. The process of claim 47 wherein the hydrocarbon or alcohol flowing in the central annular zone which undergoes the steam and/or CO₂ reforming reaction is a single constituent or a mixture of constituents of the following components:

methane,
ethane,
propane,
n-butane,
i-butane,
methanol,
ethanol,

propanol,
butanol,
naphtha,
gasoline,
natural gas rich in methane,
coal gas rich in methane,
landfill gas rich in methane,
flue gas rich in methane,
biomass gas rich in methane,

and wherein the combined hydrocarbon and carbon dioxide gas mixture is one of the following:

a CH₄ and CO₂ mixture,
acidic natural gas rich in CH₄ and CO₂,
coal gas rich in CH₄ and CO₂,
landfill gas rich in CH₄ and CO₂,
biomass gas rich in CH₄ and CO₂,

other primary, secondary, refinery, and flue gas mixtures rich in CH₄ and CO₂.

50. The process of claim 47 wherein the central annular zone is empty and no catalyst or heating elements are contained within, with oxygen gas to flow via the central annular zone, with methane gas to flow in the most inner and outer cylinders, with the two inner membrane tubes to be made by perovskite type solid oxide membranes which consist by oxygen conducting metals mixed with inorganic metal oxides to form two opposite oxygen-ion conducting structures, with the most inner cylinder and the annular space between the inner and outer cylinders to be filled with an oxidation catalyst such as nickel, rhodium, platinum, palladium, or with an oxidative coupling metal oxide type catalysts, such as La₂O₃, MgO, PbO, Li₂O in order to conduct exothermic methane oxidation, and methane oxidation coupling reactions for production of hydrogen and carbon monoxide which is synthesis gas, or for production of ethylene, ethane, and other

C_2 compounds, with the product gases formed to exit from the outlets of the most inner and outer catalytic annular zones.

51. The process of claim 50 wherein the two inner solid oxide, oxygen conducting membrane cylinders and the methane activation catalysts within, are made by one or more of the following materials, with valence x to be less than 1 or one:

Platinum,
Palladium,
Rhodium,
Nickel,
Iridium,
Silver,
Gold,
 ZnO ,
 $Li_{1-x}Ni_xO$
 $Sr_{1-x}La_xCoO_3$
 $LaCoO_3$
 $PrCoO_3$
 $La_{1-x}Ca_xCoO_3$
Yttria stabilized ZrO_2
 $Ni-ZrO_2$
 $La_{1-x}Sr_xFeO_3$
 $La_{1-x}Sr_xMnO_3$
 $La_{1-x}Sr_xCrO_3$
 $La_{1-x}Ba_xCoO_3$
PbO and $PbO.K_2O$
NiO
 In_2O_3
 Cr_2O_3
 Co_3O_4